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Identification and Measurement of Components in Gasoline, Kerosene, and No. 2 Fuel Oil That Partition into the Aqueous Phase After Mixing

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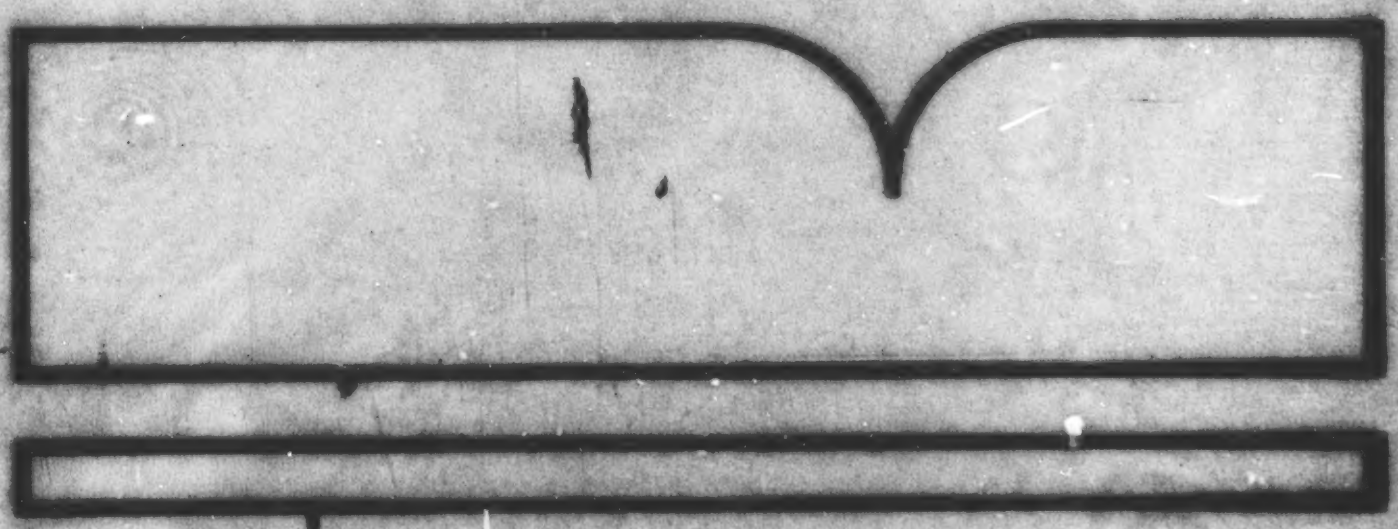

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16. ABSTRACT

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Archives of Environmental Contamination and Toxicology

The Identification and Measurement of Components in Gasoline, Kerosene, and No. 2 Fuel Oil that Partition Into the Aqueous Phase After Mixing

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Abstract. Some of the most common spills in waterways involve petroleum products, which are complex mixtures of varying compositions, depending on source and refining procedures. The tendency for components of potential toxicological significance to distribute to the aqueous phase under spill conditions needs to be determined. This paper is devoted to the chemical analysis of the water-soluble fractions (WSF) of gasoline, kerosene, and No. 2 fuel oil, which were added to drinking water and extracted into the aqueous phase under simulated field conditions. Initial aspects of the study dealt with the identification and distribution of the major components to the aqueous phase using pentane extraction and capillary column gas chromatography/mass spectrometry (GC/MS) for analyses. Results show that at least 95% by weight of the components in the WSF of each fuel sample were aromatic compounds having 6 to 13 carbons.

Background and Introduction

A variety of chemicals contaminate water on a sporadic basis or in very limited areas. Spills of certain bulk products occur with sufficient frequency to warrant developing the toxicological information necessary to establish emergency guidance as to the levels of exposure which humans can tolerate for varying lengths of time. Spills often have impact on a local water supply of a few hours to a few days and higher concentrations may be generally, but not always, tolerated.

The large-scale use of petroleum products poses a serious threat to the safety of both oceans and inland waterways. Tanker spills and offshore platform blowouts are capable of inflicting tremendous damage to huge expanses of the marine environment. Heating fuels and gasoline from boats and automobiles are major sources of petroleum product pollution of lakes and rivers. Groundwater is contaminated by leakage from an increasing number of aging underground gasoline storage tanks. The scope of these forms of water pollution warrant the extensive investigation of the composition and toxicity of the water-soluble fraction (WSF) of petroleum products.

The actual composition of a pure petroleum product is dependent upon the raw source (crude oil, coal, shale oil, *etc.*), the degree of chemical modification (for example, cracking), and the physical separation method employed. Whittemore (1979), using GC/MS analysis of gasoline, found every identifiable peak in the chromatogram to be a hydrocarbon. This hydrocarbon dominance is consistent throughout all fractions derived from crude oil. However, the aromatic content of No. 2 fuel oil was reported to be less than 10% by Zürcher and Thüer (1978) but 30–32% by Bingham *et al.* (1980). Obviously, petroleum fractions of the same designation may have quite a variable composition.

More important for our purposes than pure product composition is the composition of the WSF. Zürcher and Thüer (1978) reported the WSF of No. 2 fuel oil being dominated by alkylated benzenes

[1] To whom inquiries should be addressed

and naphthalenes, with the amount and distribution apparently dependent on the concentrations in the original distillate fraction. Montz *et al.* (1982) found the WSF of two-cycle outboard motor exhaust to be almost exclusively alkylated benzenes, with the unidentified components being partial oxidation products. Anderson *et al.* (1974) made comparisons of the WSFs of crude oils and refined oils. They discovered that the WSFs of crude oils had higher total hydrocarbon concentrations and higher concentrations of light aliphatics and substituted benzenes than those of refined oils. The WSFs of synthetic oils may differ greatly from the WSFs of crude oil distillates. Dauble *et al.* (1982) analyzed the WSF of a coal liquefaction product and determined it to be almost exclusively phenols.

An additional concern regarding petroleum product pollution is that some of the components of the WSF may react to form more hazardous byproducts. Reinhard *et al.* (1976) showed that aromatic hydrocarbons are readily chlorinated when exposed to highly chlorinated waters.

The threat posed by petroleum product pollution depends upon the length of time the environment is exposed to it. Several forms of weathering disperse or eliminate components of this pollution in the aquatic environment. The two most important in the removal of volatiles from an oil slick are evaporation and dissolution. Researchers do not agree on which is of greater importance. This can be elucidated by observing two compounds of the same volatility but different solubilities. If evaporation is dominant, the two compounds will be depleted from the slick equally. If dissolution is the dominant mode of removal, then the more soluble compound will be depleted more rapidly. Boehm *et al.* (1982) and Brooks *et al.* (1981) each observed almost equivalent losses of aromatics (high solubility) and alkanes (low solubility), attributing this to a dominance by evaporation. On the contrary, Zürcher and Thüer (1978) observed a rapid loss of isopropylbenzene compared with that of nonane, attributing this to dissolution being the dominant mode of removal. Surface waters containing dissolved petroleum components are depleted by evaporation over short periods of time. Gschwend *et al.* (1982) found that it took about two days for the alkylated benzenes from boat fuel and exhaust to be dissipated from a coastal site, the length of time predicted if evaporation were the mode of removal. They found evidence of some biodegradation of ethylbenzene and propylbenzene. Zürcher and Thüer (1978) studied fuel-contaminated ground water, observing pristane and phytane but not the corresponding C_{18} and C_{20} n-alkanes. This suggests possible biological degradation. Boehm *et al.* (1982) determined "that biodegradation was nearly inoperative in the open sea except in very special microenvironments." Model experiments conducted by Zürcher and Thüer (1978) demonstrated that higher boiling components of No. 2 fuel oil adsorbed into kaolinite particles suspended in water. Finally, where water turbulence exists, agglomeration of oil droplets occurred, potentially leading to oil sedimentation.

More important than the number of compounds found in the WSF of petroleum products is the toxicity of those that are found. Tests of the mutagenicity of pure products revealed the following order of toxicity: coal liquefaction > shale oils > crude oils. Polynuclear aromatic amines present in synthetic oils are responsible for their greater mutagenicity. Most of the mutagenicity of crude oils results from polynuclear aromatic hydrocarbons (Guerin *et al.* 1980). Blumer *et al.* (1973) stated that the acute toxicity associated with an oil spill is derived from the WSF. Since polynuclear aromatics are much less water-soluble than benzenes and naphthalenes, their role in the toxicity of an aquatic environment is greatly attenuated. Results of preliminary bioassays by Anderson *et al.* (1974) indicated that naphthalene and alkyl naphthalenes were 3 to 10 times more toxic (acute) to test animals than benzene and alkyl benzenes, which would support their finding the WSFs of naphthalene-rich refined oils more toxic (acute) to crustaceans and fish than the WSFs of crude oils. Giddings and Washington (1981) found the WSF of synthetic oils much more toxic to algae than the WSF of natural oils. They reported the WSF of a coal liquefaction product had almost 50× the total organic carbon concentration of the WSF of a petroleum product. This was probably due to a large amount of phenols, aromatic amines and other highly soluble polar aromatics present in coal liquefaction products.

When considering the hazard posed by petroleum product pollution, the complexity of a real situation compared to controlled laboratory studies cannot be ignored. Biological activity may be elicited from a combination of compounds, when the compounds individually elicit none. Also, these products are complex mixtures of potentially reactive substances. The byproducts formed when these substances are released into an aquatic environment may differ tremendously from the original substances in their degree of toxicity.

In the present paper, a study was designed to determine the magnitude and composition of the WSFs of unleaded gasoline, kerosene, and No. 2 fuel oil in order to answer the question as to which components of the fuel products are likely to enter drinking water supplies and be of toxicological significance. This study was conducted in real drinking

water to minimize interferences from sedimentation and biodegradation. Results from this preliminary investigation might suggest candidate compounds for future drinking water health effects studies. The WSFs were analyzed after both ½ and 17 hour equilibration times to determine the effect of evaporation on composition.

Experimental

Preparation of Internal Standard Stock Solution

An internal standard stock solution containing 1.044 ng/μL each of 1-chlorohexane, 1-chlorododecane, and 1-bromo-4-fluorobenzene was prepared in Burdick and Jackson "distilled in glass" pentane[a]. "Distilled in glass" pentane was used throughout the project for all dilutions and extractions. This stock solution was prepared and stored in a 10-mL, ground glass stoppered, volumetric flask. It was stored at −5°C in the dark.

Preparation of Petroleum Product Dilutions for GC/MS Analysis

One sample each of unleaded gasoline, kerosene, and No. 2 fuel oil were obtained from commercial sources. Approximately 200 mL were contained in 240-mL glass bottles, and were stored in the dark at room temperature. The density of each product was determined.

A dilution of each product to be analyzed was prepared in pentane. A 10-mL volumetric flask was filled to approximately 90% of capacity with pentane. Two hundred and fifty μL of the internal standard stock solution was injected under the surface of the pentane with a microliter syringe. The resulting concentration of each internal standard was 26 μg/mL. Ten μL of the desired petroleum product was injected under the surface of the pentane with a microliter syringe, and the flask was filled with pentane to the 10-mL mark. These product dilutions were stored in ground glass stoppered volumetrics at −5°C in the dark. The concentration of each petroleum product dilution was calculated from its predetermined density. Concentrations ranged from 0.71 to 0.82 μg/μL. Two μL of each dilution was analyzed by capillary GC/MS.

Preparation of Water-Soluble Fractions (WSFs)

A WSF of each petroleum product to be tested was prepared with Cincinnati tap water obtained from our laboratory tap at 26 W. St. Clair, the pH of which was about 8 and the residual chlorine ranged from 0.2–0.4 mg/L. After allowing the tap to run for at least 15 min, two 1-L water samples were collected, each in a 1-gal glass bottle. One mL of the desired product was added to one bottle. Care was taken to place the fuel on top of the water without touching the bottle side. The other tap water sample was used as a control.

Both the fuel/water mixture and its associated control were agitated on a Burrell wrist action shaker at the slowest speed. This produced a mild sloshing action meant to simulate mixing in a natural body of water. The bottles were left uncapped to allow evaporation that would be a factor in a real spill situation. Only one WSF was prepared per day to eliminate any possibility of cross contamination of volatile compounds between products. Fuel/water mixtures were agitated for 3 hr. After allowing the mixture to equilibrate for 30 min, four 43-mL aliquots each of the WSF and the control, were siphoned with a glass "U" tube from the bottom of the sample into glass, Teflon®-lined septa sealed screw cap vials. A gentle stream of air was forced through the U tube as the open end of the "U" was submerged under the surface of the water/fuel mixture to prevent any of the fuel layer from entering the opening of the tube as it passed through that layer. Similar aliquots were taken after an equilibration time of 17 hr. Centrifugation of the water layer was not performed to remove fuel that could possibly be entrained in it, since centrifugation would not be a natural occurrence in a petroleum spill situation. If our samples contained entrained fuel, then presumably so would a natural body of water, and this is what we wished the study to reflect. All WSFs were collected headspace free and stored at 4°C in the dark until the time of analysis. One WSF of each petroleum product at a given dose and its respective control were prepared for this study. Samples and controls were stored no longer than five days prior to analysis.

Pentane Extraction of WSFs

Approximately one hr prior to GC/MS analysis, a WSF or control was removed from refrigeration to allow it to reach room temperature. After ½ hr, the cap was removed and 3 mL of the sample removed and discarded. One mL of pentane was added to the remaining 40 mL in the vial. To this, 25 μL of the internal standard stock was added by injecting it into the aqueous phase below the pentane layer. Samples were extracted by shaking on a Burrell wrist action shaker for 10 min at the highest speed. After a 15 min equilibration time, 2 μL of the pentane extract were analyzed by GC/MS. Duplicate WSFs and controls were extracted and analyzed for each product and equilibrium time in the study.

GC/MS Equipment and Operating Conditions

All GC/MS analyses were performed on a Finnigan Model 3300 quadrupole mass spectrometer equipped with an Incos Model 2300 data system computer. A Carlo-Erba Fractovap 4160 gas chromatograph was equipped with a Grob-designed splitless injector and a 60 m long × 0.25 mm i.d. wall-coated-open-tubular fused silica SE-30 column. One end of the column was inserted into the MS ion source chamber just to the edge of the ion beam, by way of a transfer oven, the temperature of which was held at 270°C.

Two microliters of each fuel dilution, WSF extract, or control extract was injected with the column vent of the splitless injector closed. The column vent (20:1 ratio) was opened 30 sec after injection.

The hot needle injection technique by Grob and Grob (1979) was used for all analyses. The helium carrier gas flow rate was 3 mL/min at 25°C; the linear velocity through the GC column was 25 cm/sec with a helium head pressure of 1.2 kg/cm² (17 psi) without a flow controller. The injector temperature was maintained at 260°C. Samples were injected at 20°C by cooling the GC oven with liquid nitrogen. After a 6 min hold at 20°C, the

[a] Mention of trade names of commercial products is for identification only and does not imply endorsement by the U.S. Environmental Protection Agency.

oven temperature was programmed to 250°C at a rate of 2°C/min. Mass spectra were acquired at the rate of one spectrum per 2 sec (range: 14-450 amu at 70eV; source temperature: 90°C). Source pressure was approximately 5×10^{-6} torr when the GC column temperature was 25°C. Data acquisition was terminated after 3,900 mass spectra (130 min) were obtained.

Compound Identification and Measurement

Compounds were identified by computer spectral matching techniques, comparing unknown spectra to those in the EPA/NIH/NBS library which contains 38,728 mass spectra. An in-house library containing 215 standard compounds that have been analyzed in our laboratory was also used.

Because of the enormity of the task of obtaining and analyzing quantitative standards for all of the constituents of the petroleum products and their WSFs, an alternate method was used to calculate the approximate weight percent of each of many classes of compounds in the products themselves and their WSFs.

A tabulation of peak identifications revealed that the products and their WSFs contained exclusively hydrocarbons. All peaks were grouped by number of carbons and basic structure (aliphatic hydrocarbon, benzene and substituted benzenes, naphthalene and substituted naphthalenes). By summing the reconstructed ion current (RIC) peak areas of the compounds in each category and dividing by the total RIC area of the chromatogram, a weight percent of each category was calculated.

Results and Discussion

The chromatograms in Figure 1 represent the comparison of two gasoline WSFs at ½ hr and 17 hr equilibration times to the product itself. The reader should notice that the largest peaks in the WSFs are not necessarily the major components of the fuel. The unleaded gasoline product contained by weight approximately 50% aliphatic and 50% aromatic compounds. However, analysis of the gasoline WSF showed that 87–95% by weight of the compounds in the WSF were aromatic. The ½ hr and 17 hr WSFs were similar with some losses of the lighter molecular weight aromatics and increased solubility of the naphthalenes in the 17 hr WSF with time. The C_{10} and lower aliphatics are generally represented in the chromatogram from scans 240–1000. The largest GC peak in the gasoline WSFs between scan 500 and 600 is toluene.

Figure 2 illustrates the distribution of aromatic compounds in gasoline and its WSF by carbon number. Examples of aromatics by carbon number are shown in Table 1. C_8 aromatics (ethylbenzene and xylenes), comprised about 35% by weight of the total constituents measured in the WSF. Toluene (C_7), and C_9 substituted benzenes (C_9) each accounted for 20–30% by weight of the WSF. Benzene (C_6) accounted for 3–5% by weight. In every case, these weight percents of components in the WSFs were much higher than in unleaded gasoline itself.

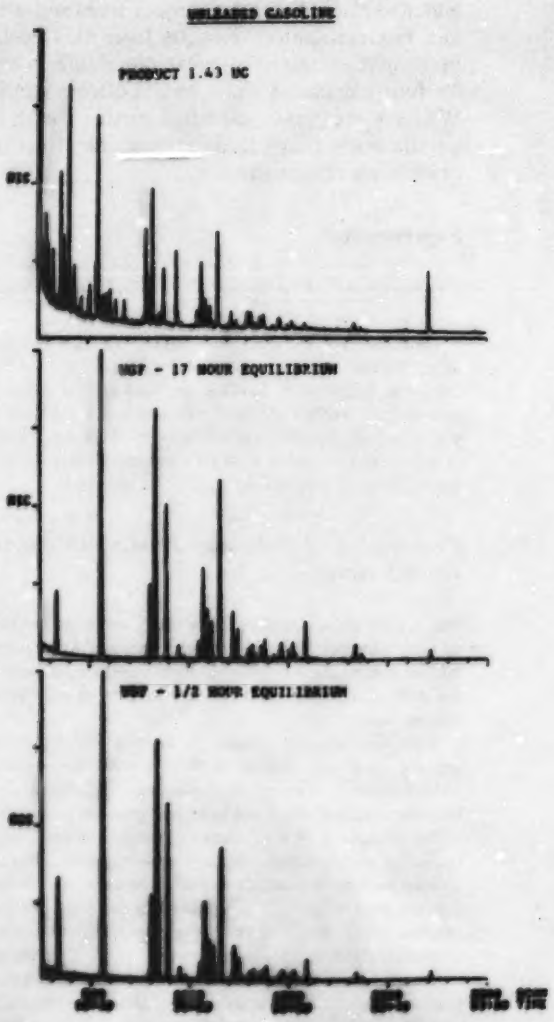


Fig. 1. Reconstructed ion chromatograms showing the comparison of two gasoline WSFs at ½ hr and 17 hr equilibration times to the product itself

The chromatograms of kerosene and its WSFs displayed as Figure 3, show a similar result as with the gasoline. Again, the largest peaks in the WSFs were not major components in the product. Nearly 70% by weight of the kerosene product consisted of aliphatic compounds, yet less than 1% of its WSF was aliphatic and 99% of this WSF was aromatic.

Figure 4 shows the distribution of aromatic compounds in the kerosene product and its WSFs. C_{10} and C_{11} aromatics were the major constituents of the WSF. Together, they accounted for more than 50% by weight of the WSF. Because kerosene is a higher boiling petroleum product than gasoline, more higher molecular weight constituents were

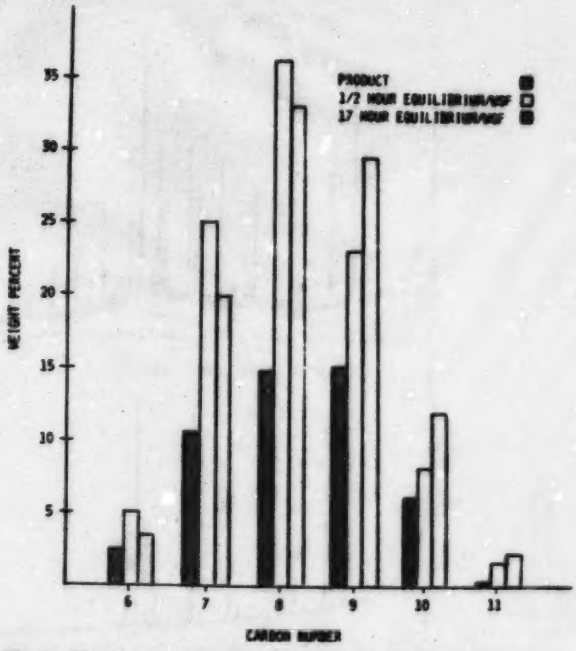


Fig. 2. Distribution of aromatic constituents in unleaded gasoline and its WSFs

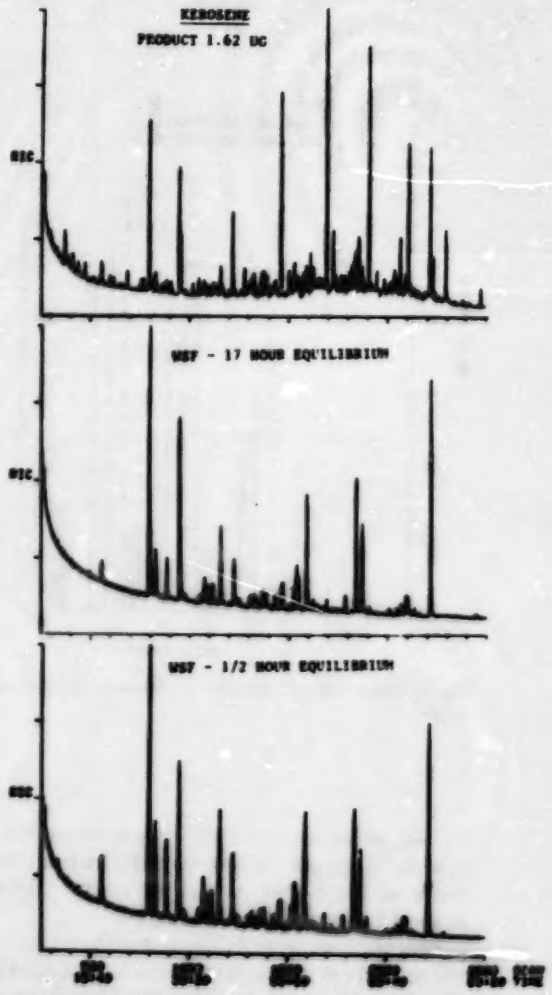
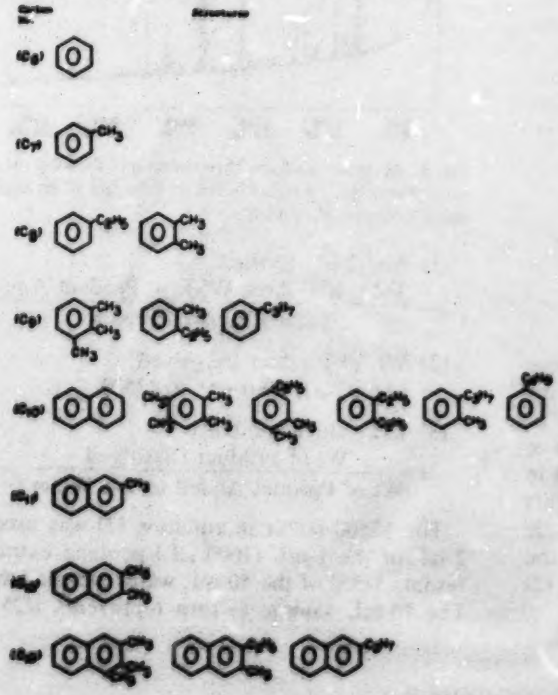


Fig. 3. Reconstructed ion chromatograms showing the comparison of two kerosene WSFs at ½ hr and 17 hr equilibration times to the product itself

Table 1. Examples of types of aromatics detected in gasoline, kerosene, and No. 2 fuel oil by carbon number



measured in both the WSFs and the product. The heavier aliphatic hydrocarbons $>C_{12}$ which were measured in the kerosene product showed very limited solubility in the water and remained as a layer on the water.

Chromatograms from the analyses of fuel oil No. 2 and its WSFs, Figure 5, were consistent with the gasoline and kerosene findings. Only aromatics were measured in the WSFs even though almost 50% by weight of the fuel oil itself was composed of aliphatics.

The distribution chart in Figure 6 for fuel oil No. 2 and its WSFs shows that 40% by weight of the WSFs was C_{11} aromatics, mostly methylnaphthalenes. C_{10} and C_{12} aromatics comprised about 25%

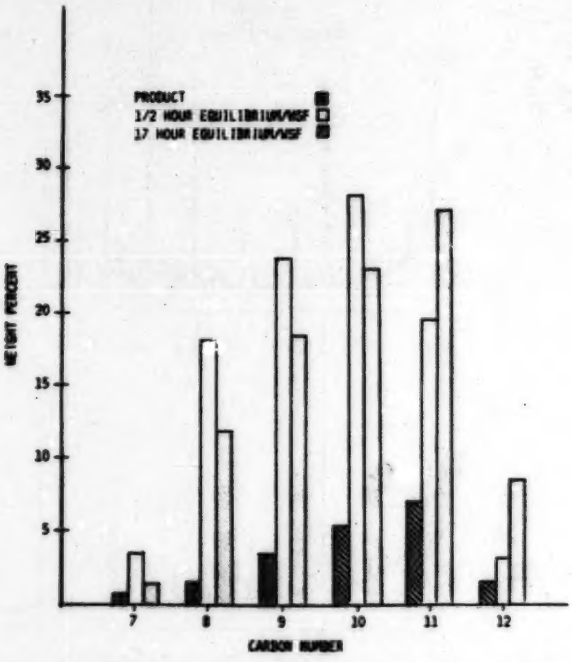


Fig. 4. Distribution of aromatic constituents in kerosene and its WSFs.

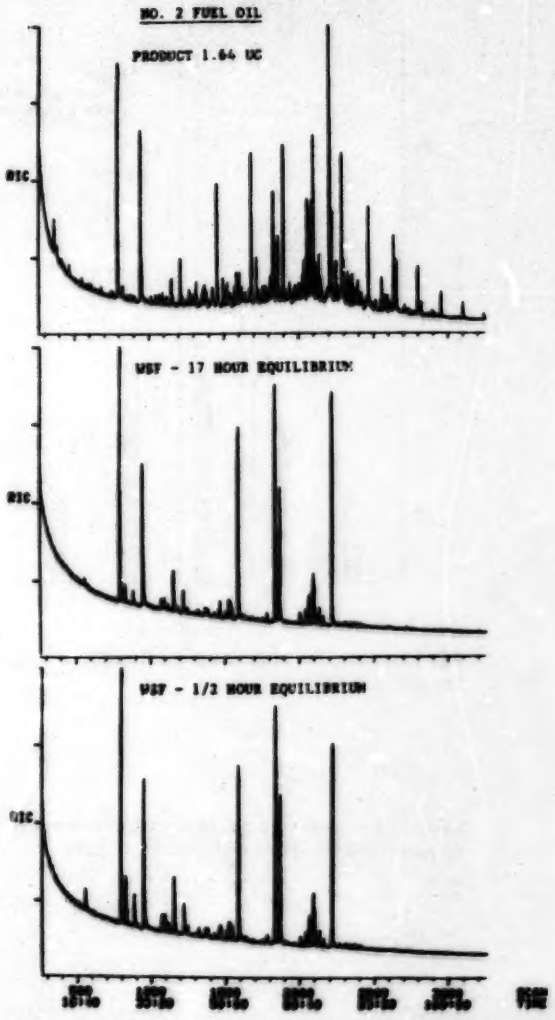


Fig. 5. Reconstructed ion chromatograms showing the comparison of two No. 2 fuel oil WSFs at ½ hr and 17 hr equilibration times to the product itself

by weight of each WSF. Since fuel oil No. 2 represents a higher boiling petroleum fraction, even more of the higher molecular weight constituents than in kerosene were measured.

Calculations were made to determine the approximate percent by weight of each product that was dissolved in tap water for the foregoing experiments. The results are indicated below:

	½ hour	17 hour
Gasoline	16.0%	12.0%
Kerosene	1.0%	0.7%
Fuel oil No. 2	1.1%	1.0%

Estimates of percent solubility by weight were determined by first comparing the total reconstructed ion current (RIC) chromatogram area of the product to the total RIC chromatogram area of the WSF sample extract, to calculate an amount in the 2 μL analyzed as shown in equation (1). This amount was related back to the original 1-L sample and compared to the amount of fuel added to the water before mixing according to equations (2) and (3).

$$(1)\ \text{Amt/2 } \mu\text{L Extract} = \frac{\text{Total RIC Area WSF} \times \text{Product Amt}}{\text{Total RIC Area Product}}$$

$$(2)\ \text{Wt. of Product Dissolved} = (\text{Amt/2 } \mu\text{L Extract}) \times 12500$$

$$(3)\ \%\ \text{Product Solubility} = \frac{\text{Wt of Product Dissolved}}{\text{Wt of Product Added to 1-L Water}} \times 100$$

The 12500 factor in equation (2) was used since 2 μL of the 1-mL (1000 μL) pentane extract represents 1/500 of the 40-mL water sample analyzed. The 40-mL sample in turn represents 1/25 of the

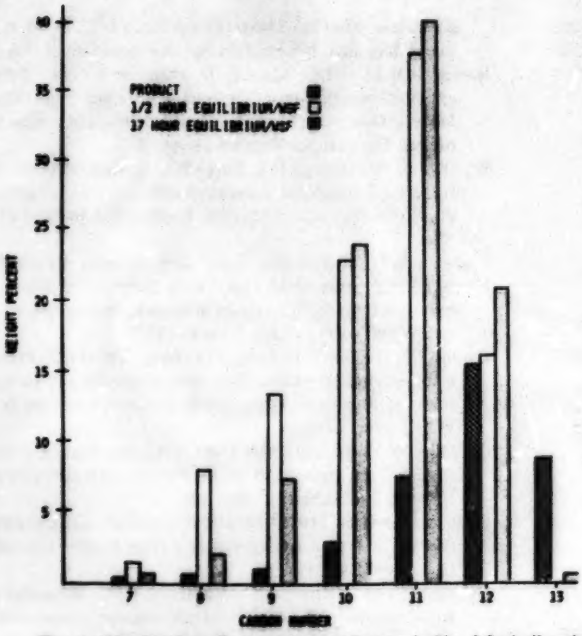


Fig. 6. Distribution of aromatic constituents in No. 2 fuel oil and its WSFs

original 1-L sample. Therefore, the 2-μL sample for GC/MS analysis was 1/12500 of the original sample.

To demonstrate the occurrence of petroleum-type products in surface drinking water supplies, Table 2 shows the results of analysis of a drinking water sample by closed-loop stripping (Coleman *et al.* 1981). Identifications of compounds were confirmed by comparing GC/MS relative retention time and mass spectral characteristics to those of authentic standards. Concentrations were calculated based on GC/MS response factors of individual standards using the internal standard method of quantitation.

Table 2. Petroleum-Type products detected in Cincinnati, Ohio drinking water, February 1980

Compound	Concentration (ng/L)
Benzene	843
Toluene	231
Ethylbenzene	36
1,3-Dimethylbenzene	92
1,4-Dimethylbenzene	92
Styrene	24
1,2-Dimethylbenzene	56
Isopropylbenzene	14
Propylbenzene	33
Ethyl-4-methylbenzene	49
Ethyl-3-methylbenzene	NQ[a]
1,3,5-Trimethylbenzene	36
Ethyl-2-methylbenzene	NQ
1,2,4-Trimethylbenzene	127
1,2,3-Trimethylbenzene	45
Indan (2,3-dihydroindene)	9
1,3-Diethylbenzene	14
(1-Methylpropyl)benzene	NQ
1,4-Diethylbenzene	12
5-Ethyl-1,3-dimethylbenzene	32
1-Methyl-4-propylbenzene	NQ
2-Ethyl-1,4-dimethylbenzene	31
4-Ethyl-1,2-dimethylbenzene	29
3-Ethyl-1,2-dimethylbenzene	16
1,2,4,5-Tetramethylbenzene	NQ
1,2,3,5-Tetramethylbenzene	36
1,3-Diethyl-5-methylbenzene	10
1,2,3,4-Tetramethylbenzene	24
1,2,3,4-Tetrahydronaphthalene	25
Naphthalene	5
Five C_1-C_3 substituted naphthalenes were identified with a total concentration of 12 ng/L.	

[a] NQ = not quantitated

Summary and Conclusions

The major constituents of the tested petroleum products and their respective water-soluble fractions, as classes of compounds, are summarized in Table 3. The data show that for all three fuels, aromatics comprised 50% or less of the weight of the product when analyzed directly. However, in each case aromatics comprised >93% by weight of the water-soluble fraction. The largest weight percentages of the water-soluble fractions were represented by C_9 aromatics in gasoline (35%), C_{10} aromatics in kerosene (33%), and C_{11} aromatics in No. 2 fuel oil (40%). This study indicates that the WSFs from higher boiling petroleum products, *i.e.*, crude oil, would continue to increase in aromaticity with higher contents of naphthalenes and polynuclear aromatics.

When toxicological studies are being planned or considered, this study has shown that a major constituent of concern in the product may or may not be the major constituent in the WSF. A minor constituent in the product could be a major constituent of the WSF if it has a greater solubility in water. The character and distribution of compounds or classes of compounds in the WSFs of fuels, heretofore, have not been specifically elucidated.

The authors realize and the reader should be aware that petroleum products may vary greatly due to source and refining procedures, and that this study was limited to one set of experimental con-

Table 3. Summary of major constituents of unleaded gasoline, kerosene, and No. 2 fuel oil and their water-soluble fractions[a]

	Product	Water-soluble fraction ½ hr	17 hr
Unleaded gasoline			
Alkanes + Cycloalkanes	48.9	1.3	0.6
Benzene + Substituted Benzenes	48.6	94.8	87.2
Naphthalene + Substituted Naphthalenes	1.0	2.4	6.0
Kerosene			
Alkanes + Cycloalkanes	68.6	4.5	0.5
Benzene + Substituted Benzenes	13.7	63.5	53.2
Naphthalene + Substituted Naphthalenes	5.7	29.6	44.8
No. 2 Fuel Oil			
Alkanes + Cycloalkanes	48.0	<0.5	<0.5
Benzene + Substituted Benzenes	4.5	25.8	19.4
Naphthalene + Substituted Naphthalenes	32.4	73.4	79.7

[a] Estimated weight percent

ditions. However, it seems evident that any toxicological and biologic activity testing should be concentrated on aromatic compounds, particularly C_6–C_{13} benzenes and naphthalenes. It may be feasible to use ultraviolet (UV) absorption analyses of the WSFs as a gross parameter for measuring aromaticity to correlate with mutagenic activity.

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